

N -representability and density-functional construction in curvilinear coordinates

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In practical implementations of density-functional theory, the only term where an orbital description is needed is the kinetic one. Even this term in principle depends on the density only, but its explicit form is unknown. We provide a novel solution of the N -representability problem for an extended system, which implies an explicit form for the Kohn–Sham kinetic energy in terms of the density. Our approach is based on a periodic coordinate mapping, uniquely defined by the Fourier coefficients of the metric. The density functional is thus expressed as an explicit functional of the metric tensor: since N -representability is enforced, our constructive recipe provides a variational approximation. Furthermore, we show that our geometric viewpoint is quite naturally related to the electron localization function (ELF), which provides a very informative analysis of the electron distribution. Studies of ELF, as obtained from accurate Kohn–Sham orbitals in real materials, allow an appraisal of the variational approximate density functional. We show that the value of an approximate functional—either the present geometric-based one or some previous ones based on different constructive recipes—strongly depends on the nature of the chemical bonding in the material.

I. INTRODUCTION

The celebrated basic tenet of density-functional theory (DFT)^{1–4} states that an exact description of a many-electron system is in principle possible in terms of a single scalar field, namely the electron density $n(\mathbf{r})$. The N -electron wavefunction contains instead redundant information; in extended systems, it does not even have a well defined thermodynamic limit. However, the Hohenberg–Kohn theorem¹ (upon which DFT is based) does not provide a constructive scheme: for any given N , the *exact* functional is indeed accessible only through the many-body wavefunction.

The enormous success of DFT resides in *approximate* schemes which are constructive, and do not make explicit recourse to the many-body wavefunction. These schemes—implemented using first-principles ingredients—have proved over the years their astonishingly accurate predictive power for many physical properties, in many different materials. In all these schemes the only wavefunction needed is a wavefunction of noninteracting electrons, which is uniquely defined by the manifold of the occupied Kohn–Sham (KS) single-particle orbitals,^{2–4} or equivalently by the KS one-body reduced density matrix. The eponymous density functional $F[n]$, Eq. (10) below, is the sum of a few terms: all of them but one are almost invariably approximated as explicit functionals of the density. The only term where the KS orbitals (or the density matrix) are actually needed is T_s , the kinetic energy of the noninteracting system, which is a functional of the density in an implicit way. This qualitative difference is of course responsible for most of the computer workload in practical calculations, hindering amongst other things the linear scaling of computations with the size of the system. There is therefore a quest for

approximate (though accurate enough) expressions for T_s as explicit functionals of the density.

Historically, the first approximate form for the kinetic energy of a system of noninteracting electrons in terms of their density is the Thomas–Fermi (TF) one,⁵ which predates DFT by several decades and is a very crude one; it is however exact for an extended system of free electrons. We focus here on a different class of approximations, which are—at variance with TF—variational: this feature is intimately linked to the problem of N -representability. In fact, whenever the approximate T_s coincides with the true kinetic energy of an arbitrary independent-electron wavefunction, then the variational theorem ensures that it must be no smaller than the exact T_s of the given system. The requisite of N -representability is equivalent to requiring that T_s obtains from a density matrix which is idempotent. There is clearly an infinity of idempotent density matrices, all yielding the same given density: amongst these infinite solutions of the N -representability problem, one searches for the one having the lowest T_s at the given density.

In order to provide an explicit approximate (and variational) expression for T_s one has, first of all, to provide a constructive recipe which, starting from a given density, produces an idempotent density matrix. Explicit solutions of this problem have been provided by several authors in the literature, amongst whom we only quote Harriman,⁶ Zumbach and Maschke,⁷ and Ludeña and coworkers.^{8–10} The present paper may thus be considered as a continuation and a generalization of this earlier work, where the elements of novelty are basically the following. (i) At variance with previous work, we are interested in extended systems. We therefore solve the N -representability problem for a system of N noninteracting electrons in a box of volume V , where periodic (Born-von

Kàrmàn) conditions are assumed at the boundary. Our approximate solution coincides with the exact one for the electron gas. (ii) Our construction uses in an essential way a periodic coordinate mapping, in the same spirit as the one advocated by Gygi^{11,12} in electronic structure calculations. This provides an elegant and symmetric treatment: some of the results obtained in the previous literature assume here an interesting geometric meaning. The electronic energy is variationally expressed in terms of the metric tensor as the independent variable. (iii) Our geometric approach naturally partitions T_s into the sum of two terms: very roughly speaking “bosonic” and “Pauli”. We show that these two terms coincide with the volume integrals of two local functions which are used in the literature as the main ingredients of the electron localization function^{13,14} (ELF).

Our solution of the N -representability problem—as well as the explicit approximate density functional based upon such solution—is therefore fundamentally linked in a very natural way to the ELF concept. Since ELF provides a very informative analysis of the electron distribution, the published results for real materials^{15–18}—obtained *a-posteriori* from accurate density matrices—help understanding what is good and what is bad in the approximate forms of T_s . We find that the quality of the approximation provided by our constructive recipe strongly depends on the kind of bonding involved in the many-electron system. We give evidence that both the Zumbach–Maschke recipe⁷ and our own one provide a reasonable T_s for simple metals in the pseudopotential approximation, while they significantly overestimate T_s whenever covalent bonding is present. The possible directions for improvement on this point are sketched.

The present paper is organized as follows. In Sec. II we present our novel solution to the N -representability problem, essentially based on a coordinate mapping, which transforms a reference uniform system into the actual nonuniform one. In Sec. III we apply such solution to the construction of a functional which is a variational approximation to the exact one: this functional is an explicit functional of the metric tensor. In Sec. IV we review the fundamental properties of ELF, a powerful tool used in the quantum-chemistry community to analyze the electron distribution in various real systems: we show that ELF is intimately related to basic features of the functional. Finally, in Sec. V we outline our conclusions and perspectives, based on some ELF analyses for real materials.

II. CURVILINEAR COORDINATES AND N -REPRESENTABILITY

For a system of independent electrons in a closed-shell configuration the wavefunction is a single determinant: knowledge of the one-particle reduced density matrix is equivalent to a complete knowledge of the wavefunction.

The spin-integrated matrix $\rho(\mathbf{r}, \mathbf{r}')$ is twice a projector, which indeed projects over the (doubly occupied) one-particle orbitals. We consider a system of N electrons in a box of volume V , obeying periodic boundary conditions. The average density is $n_0 = N/V$, the density is $n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$, and the idempotency condition is written:

$$\int_V d\mathbf{r}'' \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') = 2 \rho(\mathbf{r}, \mathbf{r}'). \quad (1)$$

We start with a homogeneous system of N non-interacting electrons at the same density n_0 , for which we use $\boldsymbol{\xi}$ as a space coordinate. For this system the canonical orbitals are, by symmetry, the plane waves $e^{i\mathbf{k}_l \boldsymbol{\xi}} / \sqrt{V}$, where \mathbf{k}_l are the reciprocal vectors determined by the boundary conditions. By choosing to occupy the $N/2$ orbitals of lowest energy, the density matrix is:

$$\rho_0(\boldsymbol{\xi}, \boldsymbol{\xi}') = \frac{2}{V} \sum_{l=1}^{N/2} e^{i\mathbf{k}_l (\boldsymbol{\xi} - \boldsymbol{\xi}')}, \quad (2)$$

which is obviously idempotent and yields a constant density. In the thermodynamic limit ($N \rightarrow \infty$ and $V \rightarrow \infty$ at constant n_0) the \mathbf{k}_l set becomes dense. Occupying the \mathbf{k} -vectors within the Fermi sphere ($|\mathbf{k}| < k_F$) Eq. (2) yields the well known electron-gas result:

$$\rho_0(\boldsymbol{\xi}, \boldsymbol{\xi}') = n_0 \frac{3j_1(k_F |\boldsymbol{\xi} - \boldsymbol{\xi}'|)}{k_F |\boldsymbol{\xi} - \boldsymbol{\xi}'|}. \quad (3)$$

At this point we introduce a generic curvilinear coordinate precisely of the same kind as introduced by Gygi in the field of electronic-structure calculations.^{11,12} We therefore define a twice differentiable invertible map $\boldsymbol{\xi} \rightarrow \mathbf{r}(\boldsymbol{\xi})$, periodic over V , whose Riemannian metric tensor is:

$$g_{ij} = \frac{\partial r^k}{\partial \xi^i} \frac{\partial r^k}{\partial \xi^j}. \quad (4)$$

Summation over repeated indices is understood throughout. A generic plane wave of momentum \mathbf{k} is transformed as:

$$\frac{1}{\sqrt{V}} e^{i\mathbf{k}\boldsymbol{\xi}} \longrightarrow \chi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} g^{-\frac{1}{4}}(\mathbf{r}) e^{i\mathbf{k}\boldsymbol{\xi}(\mathbf{r})}, \quad (5)$$

where $g = \det\{g_{ij}\}$, and $g^{-\frac{1}{4}}$ is the Jacobian $|\partial \boldsymbol{\xi} / \partial \mathbf{r}|$ of the inverse transformation. Notice that the orbitals $\chi_{\mathbf{k}}(\mathbf{r})$ have a \mathbf{k} -independent density, and are therefore “equidensity orbitals” in Harriman’s⁶ nomenclature. The density matrix in the new coordinates is:

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') &= \rho_0(\boldsymbol{\xi}(\mathbf{r}), \boldsymbol{\xi}(\mathbf{r}')) = \\ &= \frac{2}{V} g^{-\frac{1}{4}}(\mathbf{r}) g^{-\frac{1}{4}}(\mathbf{r}') \sum_{l=1}^{N/2} e^{i\mathbf{k}_l [\boldsymbol{\xi}(\mathbf{r}) - \boldsymbol{\xi}(\mathbf{r}')]} \end{aligned} \quad (6)$$

The corresponding transformed density is

$$n(\mathbf{r}) = n_0 g^{-\frac{1}{2}}(\mathbf{r}). \quad (7)$$

In the novel coordinates we thus have a nonhomogeneous system, with the same average density as the homogeneous one, and whose density matrix is idempotent by construction.

We are now ready to attribute physical content to the above mathematics. Suppose that the density $n(\mathbf{r})$ of an electronic system is given. Then we may look for a coordinate transformation $\boldsymbol{\xi} \rightarrow \mathbf{r}(\boldsymbol{\xi})$ which maps the uniform density into the given density: a necessary and sufficient condition is Eq. (7). The solution is nonunique, since several different maps share the same Jacobian $g^{-\frac{1}{2}}$: we will argue below about an optimal solution, using a variationally adaptive metric in the sense of Gygi.^{11,12} Replacement into Eq. (6) yields the explicit form:

$$\rho(\mathbf{r}, \mathbf{r}') = \frac{2}{N} n^{\frac{1}{2}}(\mathbf{r}) n^{\frac{1}{2}}(\mathbf{r}') \sum_{l=1}^{N/2} e^{i\mathbf{k}_l[\boldsymbol{\xi}(\mathbf{r}) - \boldsymbol{\xi}(\mathbf{r}')]} \quad (8)$$

In one dimension the solution of Eq. (7) is unique, and we get here the periodic analogue of the Harriman construction.⁶ In three dimensions, our result is related to the work of Zumbach and Maschke,⁷ the differences being that we deal with periodic systems, and we provide a more general explicit construction. A coordinate mapping, similar in spirit to the present one (and called “local scaling transformation”), has been previously introduced by Ludeña and coworkers for spherical atoms.⁹

III. DENSITY FUNCTIONAL

The energy of the electronic system in the external potential v_{ext} is written, within DFT, as:^{3,4}

$$E[n] = \int_V d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + F[n]; \quad (9)$$

$$F[n] = T_s[n] + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n], \quad (10)$$

where atomic Hartree units have been used. As already anticipated, basically all the available constructive approximations to DFT provide E_{xc} as an explicit functional of the density $n(\mathbf{r})$, while instead the kinetic energy term T_s is:

$$T_s = \frac{1}{2} \int_V d\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'}. \quad (11)$$

The ground electronic energy, Eq. (9), is therefore an explicit functional of the density matrix, which has to be minimized under the constraints of idempotency, Eq. (1), and electron number.

Replacement of our ansatz density matrix, Eq. (8), in the above expressions provides an upper bound to the electronic energy, explicitly expressed solely in terms of

the density and of the metric. The approximate kinetic energy is:

$$\tilde{T}_s = \sum_{l=1}^{N/2} \int_V d\mathbf{r} |\nabla \chi_{\mathbf{k}_l}(\mathbf{r})|^2. \quad (12)$$

Using then Eq. (7) of Ref. 12, the expectation value of the kinetic energy over a $\chi_{\mathbf{k}}$ orbital is the sum of two positive terms:

$$\langle \chi_{\mathbf{k}} | T | \chi_{\mathbf{k}} \rangle = \frac{k_i k_j}{2V} \int_V d\boldsymbol{\xi} g^{ij} + \frac{1}{2V} \int_V d\boldsymbol{\xi} A_i g^{ij} A_j, \quad (13)$$

where the “gauge potential” is:

$$A_i = \frac{1}{4} \frac{\partial \ln g}{\partial \xi^i}. \quad (14)$$

After summing over the $N/2$ doubly occupied states, we get

$$\tilde{T}_s[n] = \tilde{T}_P[n] + T_B[n], \quad (15)$$

where the reason for the notations will be clear in a moment.

Using Eq. (7), we cast the gauge term as:

$$T_B[n] = \frac{n_0}{32} \int_V d\mathbf{r} g^{-\frac{5}{2}}(\mathbf{r}) |\nabla g(\mathbf{r})|^2 = \frac{1}{8} \int_V d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \quad (16)$$

In the latter expression, we notice that the metric formally disappears from the gauge term, which is indeed identical to the so-called von Weizsäcker energy functional.⁴ This energy coincides with the kinetic energy of a system of noninteracting bosons in their ground state, having the given density $n(\mathbf{r})$: with this specific meaning, we may refer to T_B as to the “bosonic” energy. It is easy to prove that T_B is a lower bound to the kinetic energy T_s of a system of noninteracting fermions,⁴ and coincides with T_s only in the trivial case $N = 2$, where the Pauli principle has no effect (we are considering singlets only). In all the interesting cases, there is an excess kinetic energy T_P due to the Pauli principle:

$$T_P = \frac{1}{2} \int_V d\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} - \frac{1}{8} \int_V d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \quad (17)$$

Our expression for $\tilde{T}_P[n]$ as a function of the metric shall therefore be a variational approximation to the true excess Pauli energy T_P .

The sum over the occupied states in \tilde{T}_P is most easily evaluated if we assume a cubic box. If we define E_0 as the kinetic energy of the homogeneous system:

$$E_0 = \sum_{l=1}^{N/2} |\mathbf{k}_l|^2, \quad (18)$$

it is then easy to recast $\tilde{T}_P[n]$ as:

$$\tilde{T}_P[n] = \frac{E_0}{3V} \int_V d\mathbf{r} g^{-\frac{1}{2}} \text{tr}\{g^{ij}\}. \quad (19)$$

We further notice that in the thermodynamic limit one has:

$$E_0 = \frac{3}{10} N k_F^2 = c_F V n_0^{\frac{5}{3}}, \quad (20)$$

where $c_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}}$.

Putting all the previous formulas together and approximating T_s in Eq. (10) with \tilde{T}_s , we obtain an approximate $F[n]$ as an explicit functional of the density and of the metric tensor. Since the density—owing to Eq. (7)—is in turn a function of the metric tensor, we use the latter as the independent variable. Eventually, the electronic energy of the system, Eq. (9), is a variational explicit functional of the metric tensor $g^{ij}(\mathbf{r})$. This functional can be regarded as the periodic analogue of the one of Zumbach and Maschke,⁷ expressed in more compact form in terms of a different variable. Furthermore the explicit occurrence of the periodic metric in the \tilde{T}_P term makes feasible an adaptive optimization of the metric. Upon closely following Gygi's approach,¹² the Fourier coefficients of the periodic metric are the natural variational parameters of the problem.

Finally, we end this section just noting that in the trivial case $v_{\text{ext}}(\mathbf{r}) = 0$ all of the kinetic energy is due to T_P , since the density is constant and T_B vanishes. Furthermore the metric is the identity and the approximate kinetic energy equals the exact one: $\tilde{T}_s = T_s = E_0$, Eq. (20). The approximate functional $F[n]$ coincides with the exact one, *including* its exchange–correlation term if the exact electron–gas data¹⁹ are used therein (as usual). This suggests that the approximate functional should work reasonably well for a system close enough to the electron gas, such as a simple metal within a pseudopotential scheme.

IV. ELECTRON LOCALIZATION FUNCTION

The kinetic energy T_s can be thought of as the integral over V of a kinetic energy density $\tau(\mathbf{r})$. It is well known that the expression for $\tau(\mathbf{r})$ is not unique: we use the form suggested by Eq. (11), namely,

$$\tau(\mathbf{r}) = \frac{1}{2} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'}, \quad (21)$$

which is everywhere positive, and coincides with the choice made in the ELF literature.¹⁴ By analogy, one defines the Pauli excess energy density, after Eq. (17), as:

$$\tau_P(\mathbf{r}) = \frac{1}{2} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} - \frac{1}{8} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \quad (22)$$

This function is the main ingredient of ELF,¹³ in the formulation due to Savin *et al.*,¹⁴ who write the function as:

$$\mathcal{E}(\mathbf{r}) = \left\{ 1 + \left[\frac{\tau_P(\mathbf{r})}{c_F n^{\frac{5}{3}}(\mathbf{r})} \right]^2 \right\}^{-1}. \quad (23)$$

This function by design takes values between zero and one: several of its features are remarkable. In the homogeneous electron gas, owing to Eq. (20), the ELF equals 1/2 at any density. In a nonhomogeneous system $\mathcal{E}(\mathbf{r})$ assumes values close to its upper bound 1 in the regions of space where there is a high probability of finding a pair of electrons with antiparallel spins (or an isolated electron):^{13,14} with this meaning, we may say that $\mathcal{E}(\mathbf{r})$ close to 1 characterizes space regions where the electron distribution is “bosonic”. Conversely, $\mathcal{E}(\mathbf{r})$ is close to 0 in low-density regions.²⁰

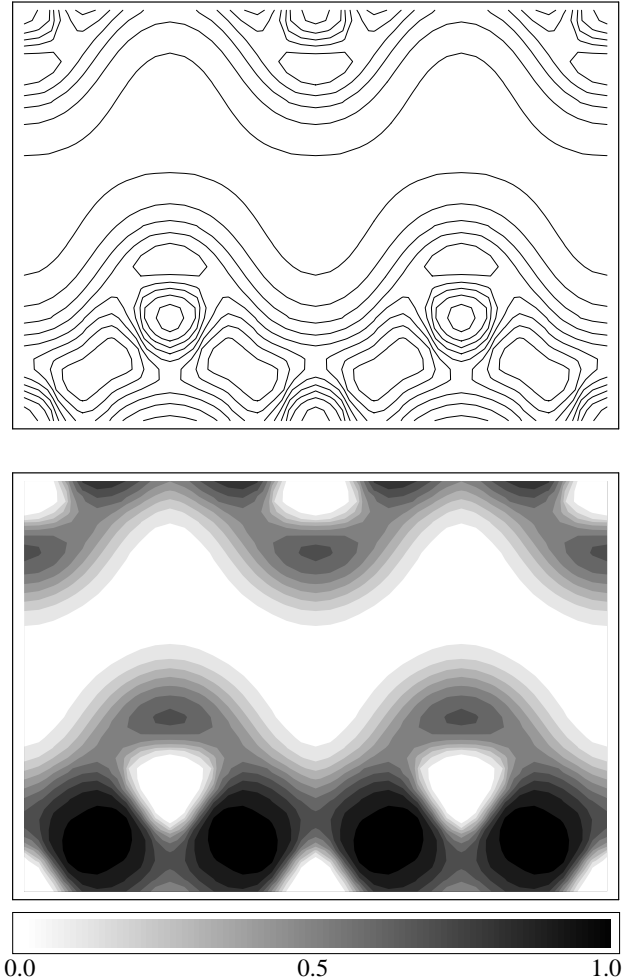


FIG. 1. Pseudocharge density contour plot (upper panel) and the corresponding ELF (lower panel) for bulk silicon in the [110] crystalline plane. The grey-scale is also shown: dark regions correspond to large ELF values. The maximum ELF value at the bond center is 0.96.

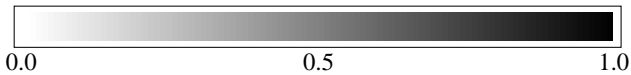
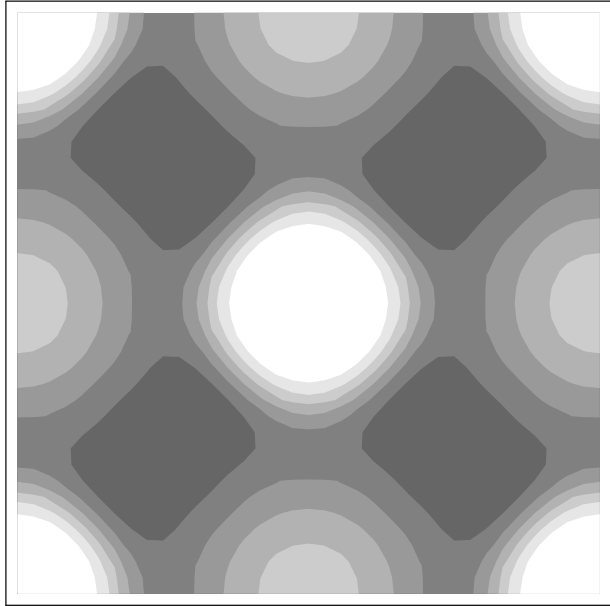
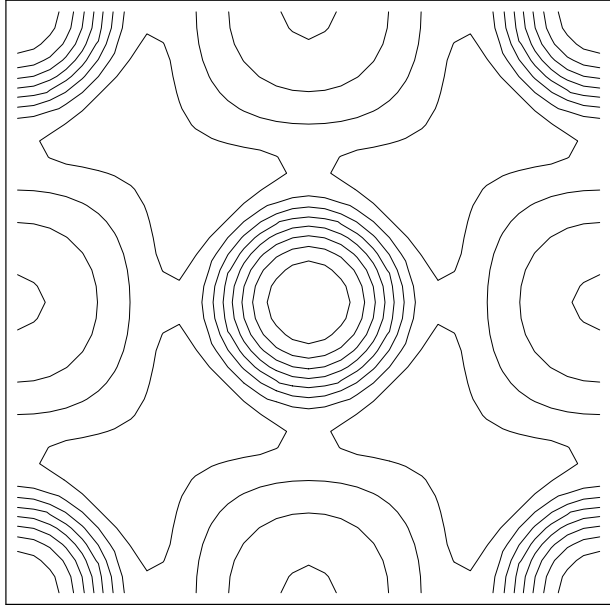


FIG. 2. Pseudocharge density contour plot (upper panel) and the corresponding ELF (lower panel) for bulk aluminum in the [100] crystalline plane. The maximum ELF value in the interatomic region is 0.61.

Detailed ELF analyses have been performed for many systems of chemical interest.^{15–17} For heavy atoms, the ELF perspicuously localizes in space the different electronic shells: furthermore, when the valence shell is considered, the ELF provides a very meaningful description of the chemical bond for many classes of compounds.^{14,18}

For the sake of simplicity, we consider only the class of *sp*-bonded materials which are accurately described

within a norm-conserving pseudopotential scheme:²¹ this class includes simple metals, covalent semiconductors, simple ionic solids, and many other disparate materials. We have in this case by construction only a single shell (the valence *sp* one of each atom involved), and the ELF allows a very meaningful analysis of the chemical bonding. Perhaps the most spectacular performance is the ability to perspicuously distinguish in a very clearcut way between metallic bonding and covalent bonding. This is illustrated in the lower panels of Figs. (1) and (2), where we plot the function $\mathcal{E}(\mathbf{r})$ for two paradigmatic crystalline materials: respectively, silicon and aluminum.

In the covalently bonded system of Fig. 1, the bond electron pairs forming the typical “zig-zag” chain in the [110] plane are clearly visible. The very dark regions in the lower panel indicate in fact the strong bosonic character of the charge density in the bond region. Actually, $\mathcal{E}(\mathbf{r})$ attains the maximum value of 0.96 at the bond center, thus indicating an extremely strong pairing between opposite-spin electrons.

A completely different picture emerges for our simple metallic system, Fig 2. The ELF plot in the lower panel shows—outside the core regions—a large grey area, which correspond to a jellium-like (or Thomas–Fermi) ELF value. Actually, the maximum value attained by $\mathcal{E}(\mathbf{r})$ is only 0.61. This is agreement with the usual picture of a simple metal, where the (pseudo) electrons are excluded from the core region, while behaving essentially as free particles in the rest of the material.²²

Comparison of the two ELF plots provides therefore the most significant and perspicuous visualization of the important *qualitative* difference between the covalent bond and the metallic one. In the two classes of materials the Pauli principle plays quite a different role. At variance with the ELF, the corresponding charge density plots, (upper panels in Figs 1 and 2) are much less informative, and do not qualitatively discriminate between the two different kinds of chemical bonds.

V. CONCLUSIONS AND PERSPECTIVES

The experience gained in investigating the ELF in real materials helps understanding the meaning and the limits of the approximate density functional such as the Zumbach–Maschke⁷ one, as well as of the generalization proposed here in Sec. III.

Our explicit ansatz of Eq. (8) leads to the Pauli excess energy \tilde{T}_P of Eq. (19). It is interesting to see the consequences for the ELF, since the ansatz clearly leads to replacing the Pauli excess energy density, Eq. (22), with

$$\tilde{\tau}_P(\mathbf{r}) = \frac{E_0}{3V} g^{-\frac{1}{2}} \text{tr}\{g^{ij}\} = \frac{1}{3} c_F n_0^{\frac{5}{3}} g^{-\frac{1}{2}} \text{tr}\{g^{ij}\}, \quad (24)$$

where the thermodynamic limit, Eq. (20), has been used. Considering now the inequality

$$\frac{1}{3} \text{tr}\{g^{ij}\} \geq [\det\{g^{ij}\}]^{\frac{1}{3}} = g^{-\frac{1}{3}} = \frac{n^{\frac{2}{3}}(\mathbf{r})}{n_0^{\frac{2}{3}}}, \quad (25)$$

we get for the approximate Pauli energy density the lower bound:

$$\tilde{\tau}_P(\mathbf{r}) \geq c_F n^{\frac{5}{3}}(\mathbf{r}). \quad (26)$$

Comparing with the ELF definition, Eq. (23), one easily realizes that even the optimal choice of the metric tensor will unavoidably provide values of $\mathcal{E}(\mathbf{r})$ which are smaller than 1/2 everywhere.

In this work we have shown that a fundamental link exists between N -representability, approximate explicit functionals, and ELF. This link emerges very naturally within the geometric approach upon which our work is based. The same geometric approach, however, also indicates very clearly the limits of the approximate form of the kinetic energy for real materials which we have found here. In fact the final considerations of the previous paragraph imply that our constructive recipe, as well as the previous one of Zumbach and Maschke,⁷ are a good approximation only for systems where the bonding is metallic, while it necessarily overestimates the kinetic energy (and the total energy) whenever covalent bonding is present. Looking more closely, this major limitation owes to the occurrence of equidensity orbitals in our ansatz density matrix, Eq. (6), which occurrence can be further traced back to the choice of the uniform electron gas as the reference system upon which we perform the coordinate transformation.

This naturally suggests the directions for improvements: one should start from a reference model system other than the uniform electron gas, having instead some covalent bonding features already built in. Interestingly, the use of a model reference system designed to reproduce—after coordinate mapping—some desirable features of the real one has been proposed in the most recent work of Ludeña and coworkers.^{9,10} These authors, however, focus on a spherical atom having several electronic shells: here instead we are discussing a condensed system with only one valence shell, within a pseudopotential scheme.

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